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TITLE A SIMULATION STUDY OF INTERFACES IN Ni, Al, AND Ni₃Al WITH
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A Simulation Study of Interfaces in Ni, Al,
and Ni₃Al with and without Boron

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ABSTRACT - Atomistic simulations of free surfaces and [001] symmetric tilt grain boundaries in pure Ni and Al and the intermetallic, Ni₃Al, are presented. In the vicinity of the grain boundary, we show the existence of a rapidly decaying oscillatory strain which is similar to that observed at free surfaces. The total expansion or excess volume associated with the grain boundary is shown to be proportional to the grain boundary energy. The atomistic structures of the simulated grain boundaries have been analyzed in terms of the structural unit model, which is found to be of limited utility in the case of the intermetallic. Preliminary results show that boron segregates more strongly to grain boundaries than to free surfaces. Boron segregation strengthens the grain boundary but has little effect on grain boundary structure other than a small local expansion.

1. Introduction

It is well known that grain boundaries can have pronounced effects on the physical properties of materials (mechanical properties, corrosion resistance, fracture path, resistivity, etc.) [1]. Accordingly, a great deal of effort has been expended in trying to understand the structure, energetics and properties of grain boundaries. As attested to by the papers presented in this volume, significant experimental and theoretical progress has been made in understanding grain boundaries in pure systems. While similar progress is being made in understanding grain boundaries in alloy systems, this area is much less developed.

In the present report, we summarize our recent results on atomistic simulations of grain boundaries in the ordered alloy Ni₃Al [2,3]. Understanding grain boundaries in this material is of particular importance since intergranular fracture limits the applicability of this otherwise promising material [4]. In order to put these results into perspective, additional simulations were performed on grain boundaries and surfaces in pure Ni and Al. A number of features of the free surfaces and grain boundaries are found to be in common. Similarly, many features of grain boundaries in the ordered alloy may be understood in terms of the results on pure Ni and Al grain boundaries. Finally, we consider the effect of boron segregation on the strength of grain boundaries in Ni₃Al.

The simulation results presented herein were obtained by first generating ideal symmetric tilt [001] grain boundaries [2,3] or free surfaces [5,9]. The resultant ensemble of atoms was then allowed to relax via a steepest descent, energy minimization algorithm. Periodic boundary conditions were employed in the two orthogonal directions co-planar with the interface. For the grain boundary calculations, the surfaces, which were at least 80 atomic layers away from the boundary, were left free. The interactions between the atoms are described by "local volume", embedded atom-like, potentials [6]. These "local volume" potentials consist of two parts: a pair potential part and a local density part. Due to the inclusion of the local density dependence, these "local volume" potentials are able to treat the large local density deviations associated with defects such as vacancies and free surfaces. Although these potentials are empirical in nature (they are fit to a wide range of thermodynamic and defect data), they are in good agreement with the experimentally determined structures and energies of metallic surfaces [5]. In contrast, traditional pair potentials do not even account for the grossest feature of the relaxed surface structure (i.e. the outermost layer of atoms should relax inward, toward the bulk). In the present work, this "local volume" approach has been applied to Ni, Al (see Ref. 6 for details), and B. In order to obtain boron-metal potentials, the "local volume" potentials were fit to thermodynamic/structural data obtained from experiment and Linearized Muffin Tin Orbital (LMTO) calculations [7]. However, it should be noted that the boron potentials [8] do not take into account directional bonding and hence, must be viewed as preliminary.

The strain field associated with the relaxation of a free surface was found to show oscillations. Figures 1 a and b show the oscillations in the normal strain field component perpendicular to the interface, ϵ_{zz} , for the (210) surface of Al [9,10] and the (210)/[001] $\Sigma=5$ grain boundary in Figures 1 a and b, respectively. This strain component was calculated as

$$\epsilon_{zz}(i,j) = (d_{ij} - d_0)/d_0 \quad (1)$$

where d_{ij} is the spacing between the i^{th} and j^{th} atomic layers parallel to the interface, and d_0 is the interlayer spacing in the perfect crystal. For the (210) surface of Al, the first layer contracts (27%) and the second and third layers expand. The oscillation is characterized by a period of 3 layers, or roughly $0.67 a_0$ (where a_0 is the lattice constant). The oscillation decays roughly exponentially into the bulk (see Ref. [5]). The period of the oscillation and its decay length are nearly identical for the free surface and grain boundary (compare Figs. 1 a and b). This decay length (beyond which $\epsilon_{zz} < 0.01$) is found to be approximately 2 lattice parameters for nearly all of the free surfaces and grain boundaries we have examined [5].

The area under the curves in Figure 1 are the net contractions or expansions associated with the interface. The net contraction of the (210) surface is $-0.067 a_0$, while the net expansion at the grain boundary (Δz) is $+0.12 a_0$. It is interesting to note, the local contraction at the surface (i.e. the net displacement of the first layer) is $-0.062 a_0$, and the local expansion at the grain boundary, Δz^* , (i.e. the change in separation of the two closest planes) is $+0.134 a_0$. The local and net expansions for the Al grain boundaries studied are shown in Fig. 2 as a function of the tilt angle. It is clear that the local expansion varies much more erratically with angle than the net expansion. At high angle boundaries (22.62° to 61.93°) the local expansion is usually larger than the net expansion by a factor of two, except for special angles (i.e. low Σ values corresponding to 36.87° , 53.13° , and 22.62°). Fig. 2 also shows that the net expansion varies much more smoothly with grain misorientation than does the local expansion. In a classic TEM experiment, Pond and Vitek [11] have measured a net expansion of $0.05 a_0$ at a (211) grain boundary in Al. Our simulations for this grain boundary show a $0.07 a_0$ expansion.

Grain boundary energies for pure Ni and Al are plotted in Fig. 3a as a function of grain misorientation angle, θ . The general shape of these curves and the presence of cusps at (210) and (310) have been observed in previous simulations employing traditional pair potentials [12]. However, the magnitude of the energies

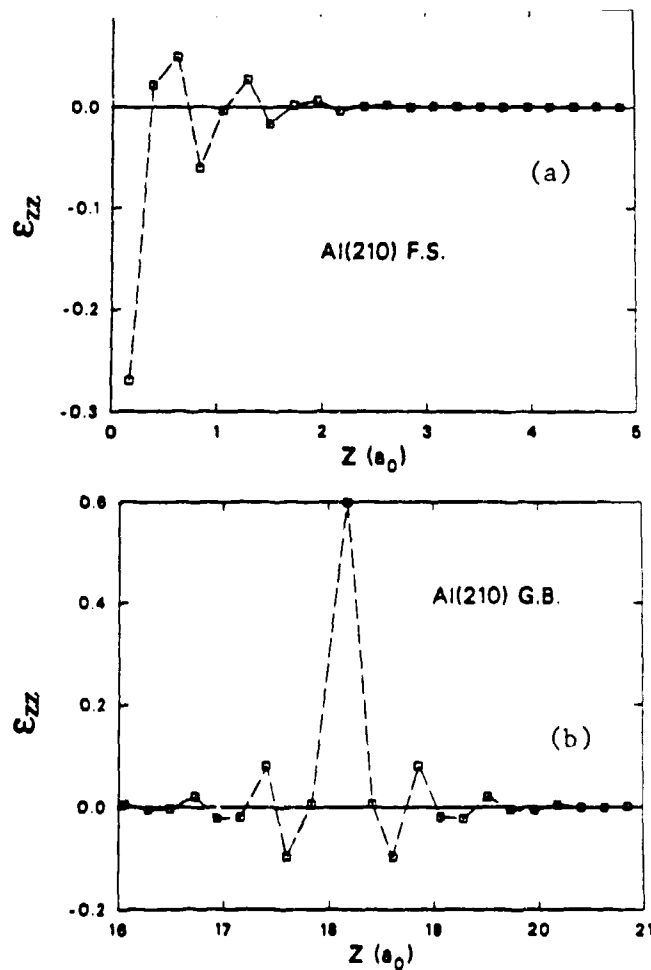


Fig. 1 The relative deviation in interlayer spacing in the direction normal to the interface, ϵ_{zz} , as a function of distance from the interface for (a) the (210) surface and (2) the (210) symmetric tilt boundary in Al.

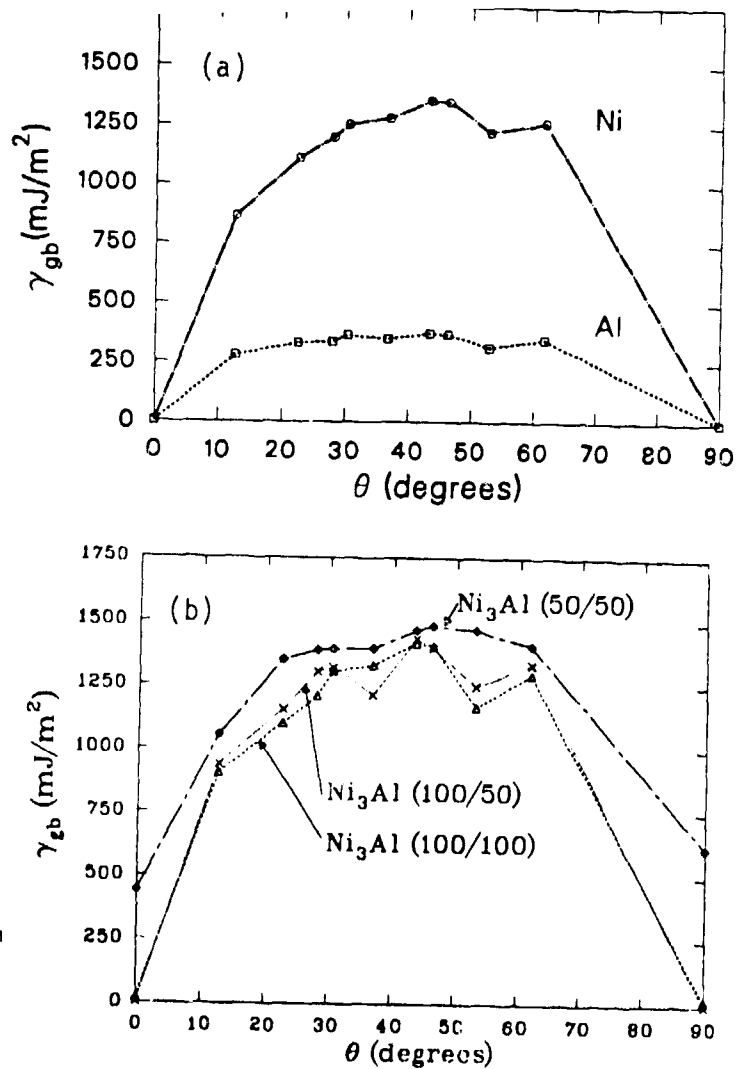


Fig. 3 The [001] tilt boundary energy of (a) Ni, Al, and (b) Ni_3Al as a function of misorientation angle.

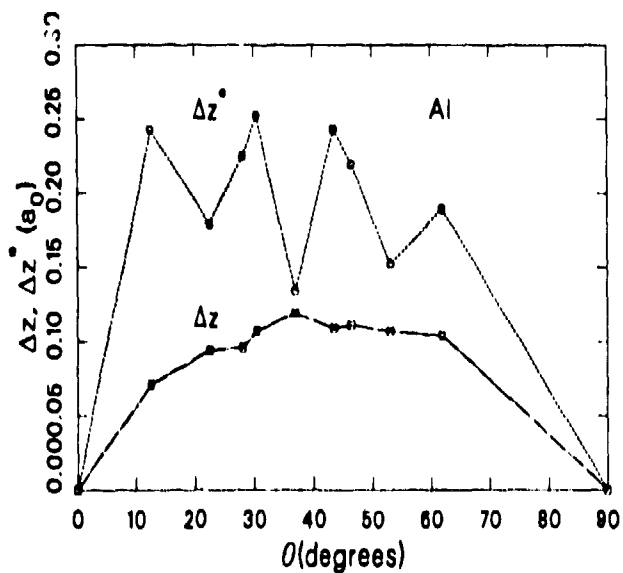


Fig. 2 The total (Δz) and local (Δz^*) expansion associated with [001] tilt boundaries in Al as a function of misorientation angle (θ).

found in the "local volume" potential simulations provide better agreement with experiment than due the pair potential simulations [12,13]. The grain boundary energy is plotted as a function of net boundary expansion, Δz , in Fig. 4a. While a strong correlation between boundary energy and net expansion is observed, no correlation was found with the local boundary expansion. A non-linear elastic analysis by Granato and Chen [14] shows that Δz should scale linearly with the grain boundary energy at small angles. This analysis predicts a ratio of the Ni to Al slopes of 3.7, compared with the simulation value of 4.0.

In the present study of pure Ni and Al [001] symmetric grain boundaries, we found that essentially all of the basic features of the structural unit model of Sutton and Vitek [15] and Wang, et al. [16] were reproduced (Fig. 5). However, the detailed atomic structure of these units were not always identical to that observed by Vitek and co-workers in their pair-potential simulations. In those few cases where the structural units differed, we find that the differences in energy are quite small.

3. Interfaces in Pure Ni_3Al

The present simulations of free surfaces in NiAl and Ni_3Al show a net contraction of the first layer contraction. However, the Al atoms in the first layer move out relative to the Ni atoms on the same plane [5], in good quantitative agreement with low energy electron diffraction data [5]. In all cases examined, the same type of rapidly decaying, oscillatory behavior in ϵ_{zz} occurs in the ordered Ni-Al alloys as in the pure metals. However, in many cases, the oscillations in the Ni and Al sub-lattices show opposite phase. For detailed discussion of the surface results, see References [5,9].

Symmetric [001] tilt boundaries in Ni_3Al have three unique grain boundary compositions (i.e. when the two grains are perfect crystals). The grain boundary composition can be described by the Ni percentage of the first layer of each grain, namely: 100/100 GB, 100/50 GB, and 50/50 GB. The 100/100 grain boundary is Ni-rich, the 100/50 grain boundary has the bulk stoichiometric, and the 50/50 boundary is Al-rich. By studying grain boundaries with different composition in otherwise perfect Ni_3Al crystals, we hope to understand the experimentally observed sensitivity of the ductility of boron doped boundaries to small variations in composition [4].

Structurally, grain boundaries in Ni_3Al are very similar to those in the pure metals. The grain boundary energy dependence on grain misorientation and boundary stoichiometry is indicated in Fig. 4b. The Al-rich grain boundaries are always higher in energy than the stoichiometric and Ni-rich boundaries. The energies of the Ni_3Al boundaries are very close to those for pure Ni. The cusp at 36.87° (210) in the grain boundary energy plot is deepest for the stoichiometric boundary while the 53.13° (310) cusp is deepest for the Ni-rich boundary. The cusps are essentially unnoticeable for the Al-rich boundaries. The Al-rich grain boundaries show larger net expansions than do the Ni-rich boundaries with the same grain misorientation. The grain boundary energy dependence on Δz is nearly identical to that for pure Ni (see Fig. 4).

The structural units of the grain boundary are generally very similar to those in the pure metals, however in some instances the structural unit in the ordered alloy is twice the size of that for the pure metal [10]. Figs. 5c-e show that for different grain boundary stoichiometries, the generic unit is the same but large distortion arises due to the different arrangement of Ni and Al atoms in the unit. Further, in some cases, the type of unit (B or B', in the nomenclature of Vitek and co-workers [15,16]) may vary with grain boundary stoichiometry or even at fixed stoichiometry as the misorientation angle is varied. Therefore, although the general features of the structural unit model are maintained in the alloy case, its utility is rather limited by the large distortions in the structural unit and by the multiplicity of types for each unit. For example, there are 10 atoms inside the B' unit in the (210) case; therefore the B' unit can have 2^{10} -1024 possible variations due to changes in the chemical identity of the atoms.

As shown above, the Al-rich grain boundaries always have the highest boundary energies and the Ni-rich grain boundaries have, on average, the lowest boundary energies. Similarly, we find the same trend in the grain boundary cohesive energy (the sum of the two surface energies minus the grain boundary energy), i.e. the Al-

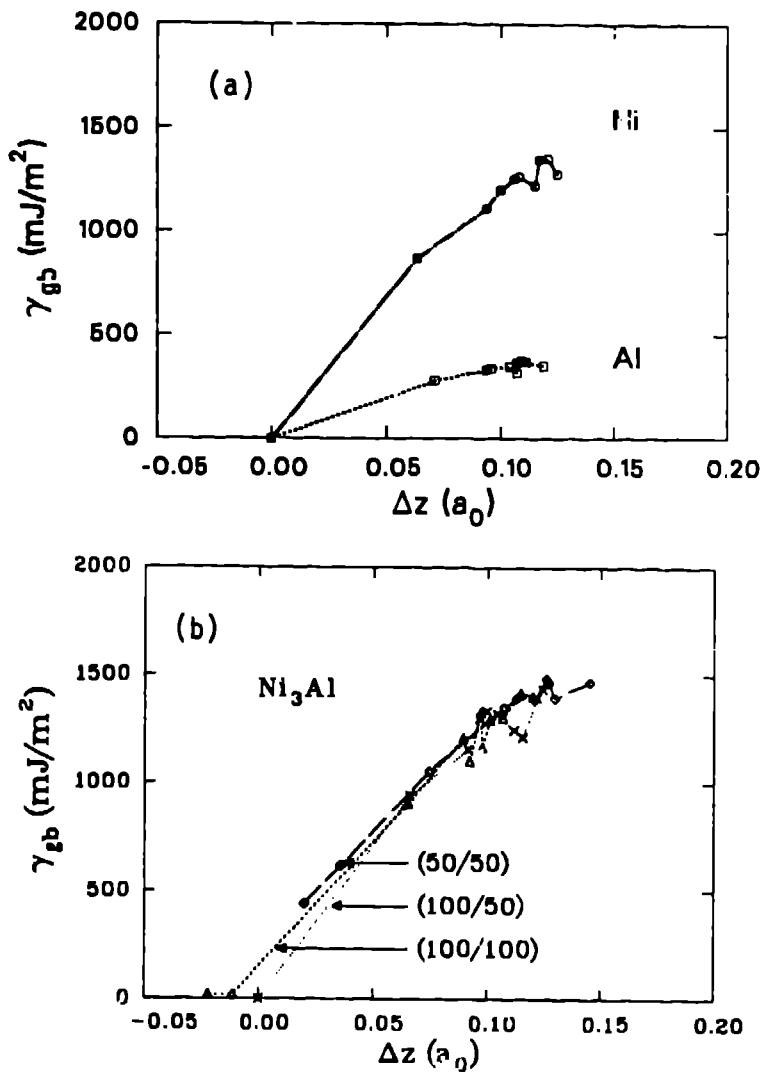


Fig. 4 The [001] tilt boundary energy as a function of total grain boundary expansion (Δz) for (a) Ni, Al, and (b) Ni_3Al .

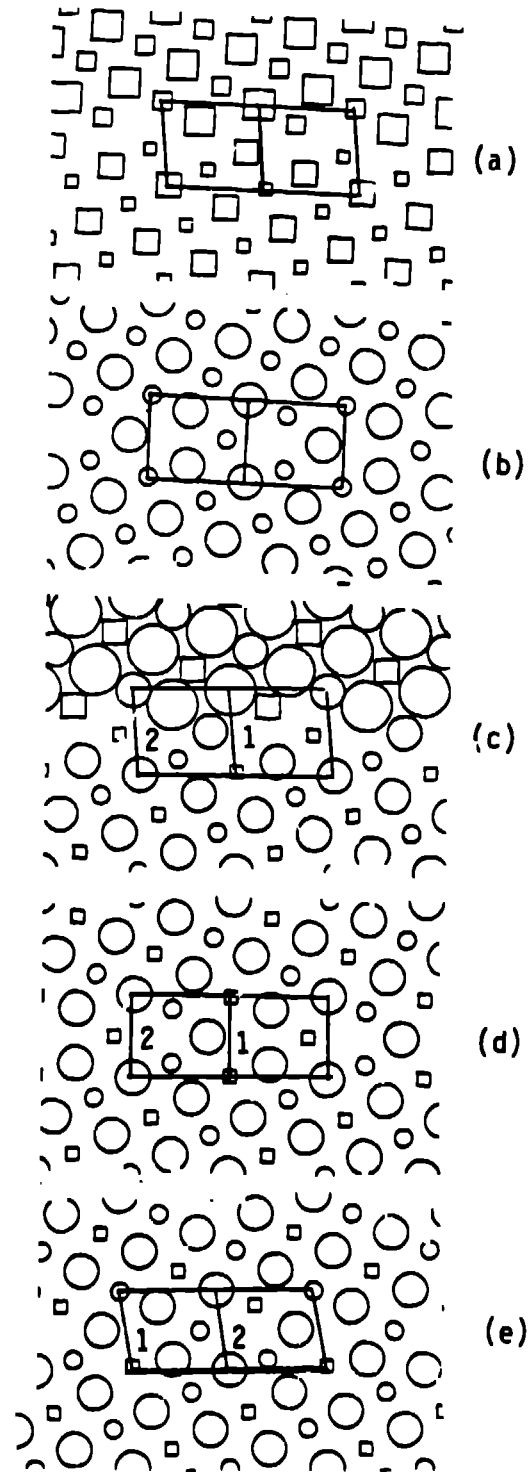


Fig. 5 The atomistic structure of the (210) symmetric tilt boundary in (a) Ni, (b) Al, (c) Ni_3Al (50/50), (c) Ni_3Al (100/50), and (d) Ni_3Al (100/100). The numbers 1 and 2 in c-e indicate the sites where boron was added in Fig. 6. The Al and Ni atoms are represented by squares and circles, respectively; the smaller symbols are displaced by $a_0/2$ into the plane of the figure. The large boxes indicate the structural units.

rich boundaries are the weakest. This cohesive energy, although small compared to the total work for fracture, has been suggested by McMahon and Vitek [17] to control the plastic work associated with fracture. A more recent analysis by Hack, et al. [18,19] shows that amount of plastic work accompanying fracture is a function of the maximum stress (σ_{\max}) which can be sustained along the fracture plane. For Ni_3Al , the value of σ_{\max} associated with grain boundaries is generally only about 80% of that for any crystallographic plane in the bulk (see Fig. 6).

4. Grain Boundaries in Ni_3Al with Boron

Starting with relaxed Ni_3Al grain boundaries, boron was either inserted into the lowest density regions in the grain boundary or substituted for Ni atoms. Subsequently, the grain boundaries were relaxed. For the limited set of boundaries currently examined, we find that boron will segregate preferentially to the low density sites in the grain boundary. Further, boron segregates more strongly to grain boundaries than to free surfaces (with energy difference of $\approx 1\text{eV/boron}$). Although we find that boron also segregates to the free surface, the ratio of the equilibrium boron concentration at the grain boundary to that on the surface is extremely large. This preference of boron for the grain boundary over the surface is in agreement with Auger experiments on Ni_3Al [4]. The change in the structure of the Ni_3Al boundary upon boron segregation is very small. Boron segregation leads to a local dilation and no drastic structural change, at least at the monolayer segregation level.

In Figure 6, we compare the maximum stress required to separate (210) grain boundaries in Ni_3Al (with and without boron) with that required to separate perfect crystal planes ((100) and (110)). In this preliminary study, the maximum stress was calculated by separating the relaxed grain boundary without further relaxation. Since the boron potentials are not as accurate as the metal potentials and due to the relatively crude manner in which the maximum stress is determined, the relative trend is more reliable than the absolute values. Fig. 6 clearly shows that the perfect planes in the bulk exhibit larger values of σ_{\max} than those of the grain boundary without boron (regardless of grain boundary stoichiometry). The substitution of boron for Ni atoms at the boundary only slightly increases σ_{\max} . Insertion of a boron atom into a low density grain boundary site, on the other hand, has a much more pronounced effect on σ_{\max} . It should be noted, however, that the

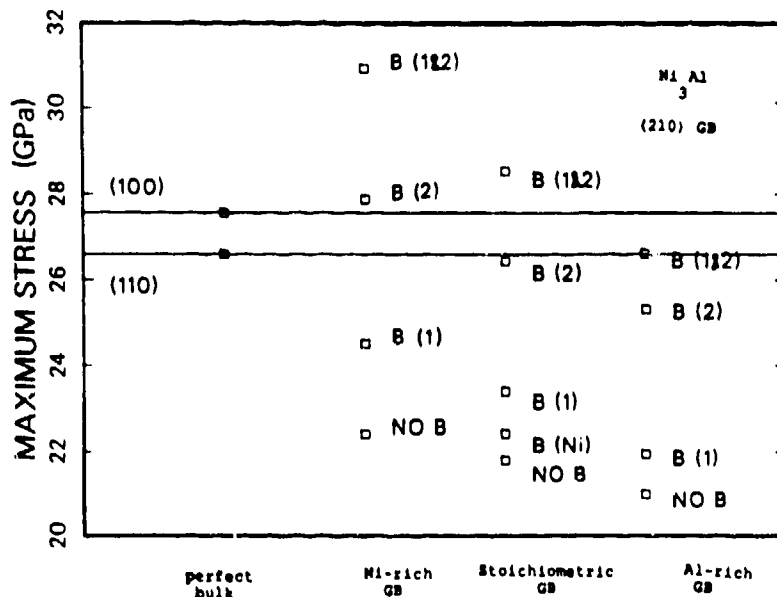


Fig. 6 The maximum stress needed to separate perfect (100) and (111) crystal planes and the (210) symmetric tilt boundary without boron or with boron (at sites 1 and/or 2 as shown in Fig. 5, or substituted for Ni).

... of the boron effect depends on exactly to which low density grain boundary site the boron segregates. Fig. 6 clearly shows that the beneficial effect of adding boron (i.e. raising σ_{\max}) increases with increasing Ni concentration at the boundary. In the case of the Ni-rich boundary, adding boron to certain sites or certain combinations of sites raises σ_{\max} for the boundary above that for certain perfect crystal planes. This implies that boron segregation can effectively make the Ni_3Al grain boundaries stronger than the bulk! Our results to date indicate, however, that this is only true when the boundaries are Ni-rich. This result, coupled with the recent simulation finding [20] that a small increase in the Ni concentration leads to a large increase in Ni concentration at the grain boundary, provides a very plausible explanation of the experimentally observation that boron ductilizes grain boundaries in Ni_3Al whe. there is a net bulk excess of Ni.

5. Conclusion

We have performed a series of simulations on grain boundaries and free surfaces in Ni, Al and Ni_3Al (with and without boron) using "local volume" potentials. Good agreement with existing experimental structural and energetic determinations have been obtained. The net expansion due to grain boundaries in pure metals and ordered alloys is found to be proportional to the grain boundary energy. Al-rich grain boundaries in Ni_3Al tend to have higher energies than stoichiometric or Ni-rich boundaries. Adding boron to grain boundaries in Ni_3Al increases their cohesive strength (σ_{\max}). This effect is much more dramatic for Ni-rich boundaries than for stoichiometric or Al-rich boundaries. In some Ni-rich cases, adding boron increases the cohesive strength of the boundary to such an extent that the boundaries become stronger than the bulk. Boron is found to segregate more strongly to grain boundaries than to free surfaces.

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